Real time monitoring of click chemistry self-healing in polymer composites†

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A photo-healable rubber composite based on effective and fast thiol–alkyne click chemistry as a self-healing agent prestored in glass capillaries is reported. The click reaction and its effect on the mechanical properties of the composite are monitored in real time by dynamic mechanical analysis, showing that the successful bleeding of healing agents to the crack areas and the effective photoinitiated click reaction result in a 30% storage modulus increase after only 5 min of UV light exposure. X-ray tomography confirms capillary-driven bleeding of reactants to the damaged areas. The effect of storing the click chemistry reactants in separate capillaries is also studied, and results show the importance of stoichiometry in achieving a significant level of repair of the composite. No reactant degradation or premature chemical reaction is observed over time in samples stored in the absence of UV radiation; they are able to undergo the self-healing reaction even one month after preparation.

Introduction

Structural composites and materials in general are vulnerable to ageing and service degradation, leading to various types of damage. The formation of microcracks and more importantly their propagation before they are detected and repaired can cause catastrophic failure of the material, which is a major concern particularly in safety-critical applications. In the quest to avoid materials failure, scientists have drawn inspiration from various self-repairing biological systems, such as clotting in biological tissues to stop bleeding,[1,2] and the closing of wounds in plants by vascular transport of nutrient-carrying cells that act as live repairing agents.[3–5]

The underlying objective has been to develop artificial self-healing materials, that is, materials that are able to self-repair structural damage and recover their original mechanical properties.[6–11] Numerous strategies towards self-healing in materials have been proposed to date. Most of them require an external stimulus (*e.g.* heat or light[12,13]) to trigger the healing mechanism, usually a chemical reaction, but are still widely accepted as self-healing. In "intrinsic" self-healing approaches, the healing agent forms part of the main material and typically consists of a polymer phase capable of crack reparation through molecular diffusion, chain interlocking, interconnecting or reentanglement based on reversible Diels–Alder cycloaddition,[14–17] supramolecular assembly,[18–20] and smart mendable polymers.[21–23] In its simplest form, repeatable healing is achieved through local melting of a thermoplastic in the damaged region, with the molten polymer filling the crack and interlocking with the surrounding matrix upon cooling; thus partially restoring mechanical properties.[24,25] One of the limitations of this strategy is the high viscosity of the polymer melt, which renders difficult the flow of the repairing agent to the damaged area. "Extrinsic" self-healing consists of the flow of an external healing agent (most often dual-component epoxy resin) to the main material, either stored in microcapsules[26] or microtubes,[9] or delivered through a microvascular network.[27] The microcapsules or glass tubes with prestored self-healing agent are typically embedded in a polymer matrix, and upon fracture of these vessels the self-healing agent is released into the cracked region, where it reacts and closes the cracked areas. Clearly, the flow of the healing agent, often called bleeding, is a prerequisite for this type of repairing strategy. Their relatively low viscosity compared to thermoplastics makes thermoset resins more suitable for this type of healing method; however, it is essential that the thermoset components are close to a stoichiometric balance at the point of reaction to approach the full mechanical properties of the polymer,[28] which in practice is very challenging.[29,30] In addition to these requirements, the healing process should ideally be fast and produce as much recuperation of properties as possible.

Click chemistry reactions are ideal candidates for self-healing because of their high yield (nearly 100%) and exceptionally fast reaction rates,[31] yet they have received surprisingly little attention in this context. Gragert and coauthors successfully encapsulated the standard azide/alkyne click reactants and

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embedded the capsules in a poly(isobutylene) matrix.[32] Under 150% tensile deformation the capsules were broken under shear and the click chemistry reactants released into the damaged area, where they could react and repair cracks. Reaction rates could be increased by supplying heat to the samples, reaching completion in 10 minutes at a temperature of 80 °C. Rowan reported on a polymer film (polydisulfide) with self-healing ability due to shape-memory properties combined with UV activated click chemistry reactions.[33]

Here, we present results on *in situ* monitoring of the healing of a rubber composite by the rapid formation of a cross-linked network by the UV photo-initiated reaction of click-chemistry agents. Through continuous dynamical mechanical analysis (DMA) during the self-healing process, we measure in real time the improvement in mechanical properties of the different possible configurations of the healing agents and the storing vessels. The results show an effective repair process, in which reaction stoichiometry is critical, particularly when the self-healing agents are stored separately in the composite.

Experimental section

Materials

A silicone rubber with low UV-Vis absorbance, LUMISIL® 885, was supplied by Wacker Chemie AG. The compounds for click chemical reaction pentaerythritol tetra(3-mercaptopropionate) (T), 1,7-octadiyne (Y) and 1-hydroxycyclohexylphenyl ketone (an ultraviolet-active photo-initiator (PI)) were purchased from Sigma-Aldrich and used as received. Glass capillaries (GCs) had an inner and outer diameter of 0.5 and 1.5 mm, respectively, according to microscopic observations. Prior to use, they were cut to a length of 50 mm.

Self-healing rubber composite preparation

The reactants T (0.689 g, 0.0014 mol), Y (0.3 g, 0.0028 mol) and PI (0.0297 g, 3 wt%) were mixed in a 1.5 mL Eppendorf tube. This solution was thoroughly stirred and carefully transferred into individual glass capillaries and then sealed with fast curing epoxy (Araldite), after which they could be embedded in the rubber matrix. The silicone-based matrix was prepared by mixing the two components LUMISIL® 885 at a 1 : 1 ratio by weight, stirring and degassing in a vacuum oven (VT6060P, Thermo scientific) until all trapped bubbles were released. Next, the mixture was poured into a Teflon mold covered with a mold release agent (Frekote® 700-NC™) and degassed again. To ensure that the GCs were embedded in the middle of the composite, first a thin layer of silicone rubber was semi-cured at 80 °C for 2 hours on which three GCs containing the self-healing agent were placed lined parallel to each other. A further layer of the silicone mixture was cast to cover the whole mold and the final part cured at 80 °C for another 2 hours. Reference experiments were conducted to confirm that no premature reaction inside the capillaries took place due to this curing process. The composite sample dimensions were 70 mm in length, 10 mm in width and 4 mm in thickness, with the glass capillaries roughly aligned parallel to the composite axis and 2 mm inside the matrix.

The healing agents (T, Y and PI) were firstly mixed in an Eppendorf tube with a stoichiometric ratio (2 thiols–alkyne), and later transferred to a GC with a thermocouple inside it (Fig. S1, ESI†). The changes in temperature were recorded as the GCs were exposed to an ultraviolet (UV) light source with a wavelength of 365 nm and an intensity of 0.4 mW cm^{-2} (at 15 cm) for 5 min. For comparison, GCs containing different chemical components (T–Y, T–PI, and Y–PI) were also tested under the same conditions.

UV-Vis measurements

Spectra of the photoinitiator (Irgacure 184) at 0.001 M dissolved in acetone (chromatography grade) and a 4 mm thick pure silicone piece, respectively, were recorded using a UV-Vis V-650, JASCO, Analytical Instrument spectrophotometer.

Dynamic mechanical analysis

All self-healing reactions were monitored in real time on a dynamic mechanical analyzer (DMA Q800, TA) using a dual cantilever clamp. A two-step protocol was designed. In the first stage, to break the GCs, the rubber composite was subjected to a controlled force increasing from 0 to 18 N with a ramp force of 6 N min^{-1}, and the force was released to 0 N after 1 min. This stage was repeated in order to confirm that no further breakage of the GCs would occur. The capillaries had two pre-introduced small notches at 10 mm from the capillary centre to facilitate localization of the damaged area but which are not a prerequisite for the observed recovery of mechanical properties. In the second step, the self-healing reaction was *in situ* monitored by DMA measurements at 1 Hz with 1% strain amplitude in bending. Each sample was at first fixed to the clamp and then covered by a polystyrene box. After measuring for 5 min to allow for stabilization of the sample and the equipment, the UV lamp (365 nm wavelength and 0.4 mW cm^{-2} intensity) was switched on. The lamp was turned off after 10 or 15 minutes, depending on the experiment. The DMA test was continued for an hour and the polystyrene box was removed 20 min prior to completion. The storage modulus, tan δ and temperature were recorded in real time, and used to evaluate self-healing efficiency.

X-ray computed tomography

The X-ray radiographs (projections) were scanned and collected using an X-ray computed tomograph (Nanotom 160NF, Phoenix) at 90 kV and 120 μA with a Mo X-ray target after centering and gain/offset calibration. The stack of tomograms (2000 projections) was later reconstructed into a 3D volume using commercial software (phoenix X-rays |datos|X reconstruction) based on the filtered back-projection algorithm for Feldkamp cone beam geometry. VG Studio Max Release 2.0 was used to further extract the regions of interest from the reconstructed 3D volume. The resolution was set to be 3.75 μm per voxel.

Results and discussion

Our self-healing system is generally described in Fig. 1. The click chemistry self-healing agents were pre-stored in glass

capillaries (GCs), which were then embedded in a transparent silicone rubber to form a composite. Fig. 1b shows an optical image of a typical composite sample. The objective is that upon fracture of the embedded GCs the reagents flow/bleed into the cracked area of the matrix where the click reaction rapidly takes place, forming a cross-linked network and thus repairing the crack (Fig. 1a). The click chemistry reaction chosen corresponds to a thiol–alkyne step-growth photopolymerization.[34] Briefly, in the presence of light in the UV range, four armed (thiyl radicals) thiol adds to the bireactive alkyne leading to fast polymerization and the formation of a three dimensional covalent network (Fig. 1c). Clearly, the stoichiometric ratio of the two reactive agents (thiol and alkyne) is critical to ensure complete polymerization and thus the effective formation of a cross-linked network that can restore mechanical properties.

First, the effectiveness of the UV-initiated click reaction was tested by monitoring the temperature inside a glass tube containing the self-healing agents (thiol, alkyne, and photoinitiator, abbreviated throughout this text as T, Y and PI, and color-coded blue, red and golden, respectively), with thiol and alkyne in stoichiometric ratios (Fig. S1, ESI†). Exposure to UV light (365 nm, 0.4 mW cm^{-2} intensity) resulted in a rapid temperature increase from 22 to 60 °C due to the exothermic polymerization reaction, which was nearly completed after only a couple of minutes. Reference experiments with different combinations of reactants (T–Y, T–PI, Y–PI) stored in GCs showed no temperature increase, as expected. The fact that the polymerization reaction starts immediately upon exposure to the UV source and terminates rapidly confirms that the choice of reactants is suitable for self-healing, where the time required to repair the part needs to be minimized before further crack growth occurs.

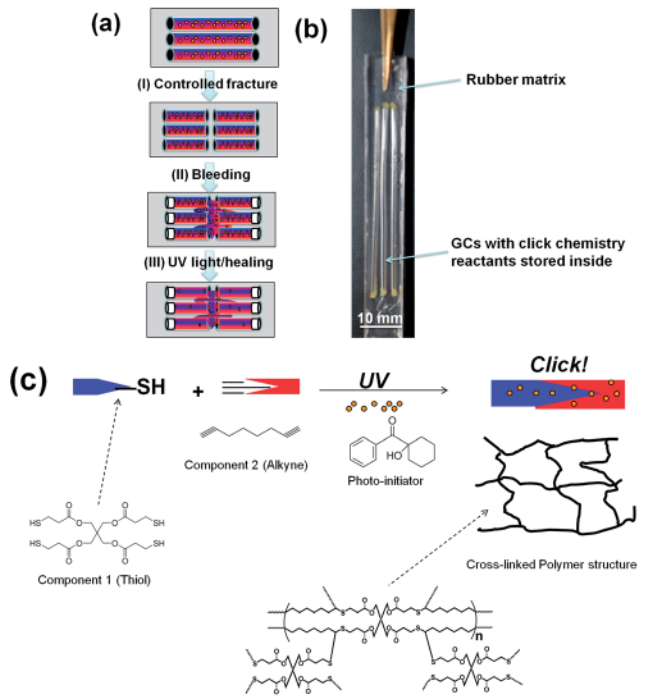

Fig. 1 Self-healing system used in this study. (a) Schematic illustration of the self-healing concept: the composite contains embedded glass capillaries with self-healing agents stored inside (thiol/alkyne/photoinitiator); upon controlled fracture of the capillaries (I), the reactants bleed to the damaged area (II) where they react in the presence of UV light and repair microcracks in the matrix (III). (b) Optical image of a typical composite sample. (c) Schematic of the photoinitiated click-chemistry cycloaddition reaction leading to the formation of a thiol–alkyne cross-linked network.

As the polymerization reaction progresses, the sample is expected to recover some of its original properties. Typically, the mechanical properties of the material are measured only before and after healing.[7,35] Here, we monitor continuously the effect of the reaction on the mechanical properties of the rubber/GC composite using a DMA to follow changes in storage modulus (for further details of dynamic mechanical analysis, see the Experimental section). First, the composite is subjected to bending deformation, typically of 2–4%, which results in controlled breakage of the GCs in the matrix and the self-release of reactants into the cracks in the matrix. In the second step, the composite is continuously deformed in dual-cantilever mode by applying a sinusoidal 1% strain at 1 Hz; thus, making it possible to monitor the evolution of sample's mechanical properties such as bending storage modulus E' and tan δ. Fig. 2 presents typical results obtained and an image of the set-up used. Immediately after the UV light source is switched on the storage modulus starts to increase from its original value of 52 MPa, rapidly reaching a plateau at 67 MPa before the lamp is turned off after 10 min. A temperature increase of a few degrees is also detected by the instrument's thermocouple in the vicinity of the sample, which provides further evidence of the successful exothermic reaction of the self-healing agents. Tan δ follows the inverse trend as E', as would be expected for a material gaining stiffness. After the first few minutes, the reaction reaches completion and no significant changes in E' (or tan δ) are observed, except for a small increase after 80 minutes due to sample cooling when the insulating cover to protect from natural UV light is removed (note that the glass transition temperature of this material is close to room temperature, see Fig. S2, ESI†).

From *in situ* measurements, the storage modulus after the self-healing reaction increases typically by 30% compared to the sample with broken capillaries (Fig. 2a). In terms of the bending modulus calculated from stress–strain curves from quasi-static dual cantilever tests (Fig. 2b), the repaired composite shows 93% recovery of bending modulus after healing compared to the pristine sample prior to glass capillary fracture. To ensure that the observed reinforcement (increased E' and reduced tan δ) is exclusively due to the click reaction, the sample with the three components and UV light was compared with two other specimens: one with only GCs and another containing capillaries filled with healing reactants but without the photoinitiator. DMA results show no healing reaction or reinforcement in these two samples (Fig. S3, ESI†), which together with background experiments in Fig. S1† confirm that all three components and UV light are required for the reaction.

Since the self-healing agents are in the whole volume of the GC containers, there could be a possible reinforcement of

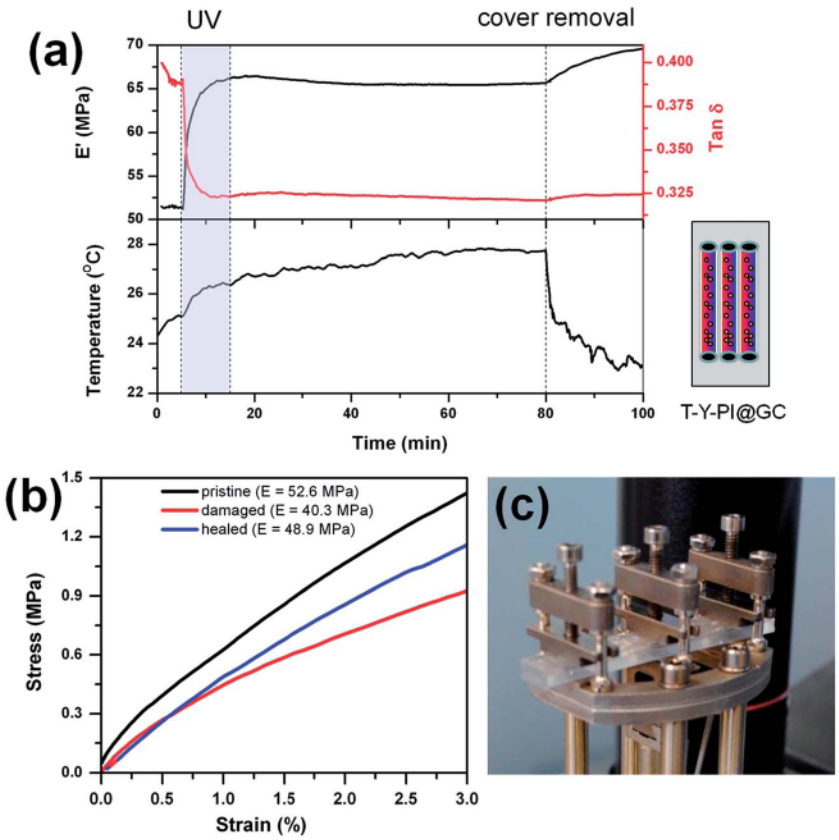

Fig. 2 (a) Plots of storage modulus E', tan δ, and temperature of the rubber composite during the self-healing reaction. A rapid increase of 30% in storage modulus is observed upon exposure to UV light (365 nm wavelength and 0.4 mW cm^{-2} intensity), with the reaction lasting less than 10 min. The schematic shows the three components for click chemical reaction stored together: thiol (T), alkyne (Y) and photoinitiator (PI), color-coded in blue, red and gold, respectively. X@GC denotes "reactant X stored in glass capillary". (b) Stress–strain curves of pristine, damaged, and healed rubber composites. The bending modulus was calculated from the linear region (0.1–1% of strain). (c) A photograph of the DMA set-up showing a sample clamped in dual-cantilever configuration.

the GCs themselves because the reactants within them are also exposed to the UV light and no doubt react rapidly to form a solid matrix inside the glass in areas distant from the crack. Yet, this possibility is ruled out in our system on the basis that the modulus of the GCs (around 50 GPa)) is much higher than that of the self-healing material (100 MPa (Fig. S2, ESI†); thus, the contribution of this soft core to the bending modulus of the glass and therefore to the composite is negligible.

The above results show the reparation of damage induced in the composite where the three click chemistry components are stored stoichiometrically in the same glass tube; however, in some cases the reagents would need to be stored separately. An engineering part prone to damage in multiple points or at frequent intervals during service, for example, would ideally need to preserve its self-healing ability after the first self-repair, which is not possible if all the reagents are stored together and hence react readily upon exposure to UV light. Thus, we study different combinations of storage of the three reactants involved in the self-healing process. Of the various possibilities, we present the results for the following samples: in the first, the reactants (T and Y) are inside the same glass capillary and the photo-initiator is dispersed in the matrix; in the second, capillaries filled with the monomer Y and the photo-initiator were alternated with capillaries containing the other monomer T and photo-initiator. In all cases, the original concentration of T and Y reactants corresponds to the stoichiometric balance. These samples are schematically shown in Fig. 3, which also includes a blank sample and that in Fig. 2, for reference.

The self-healing efficiency of these samples was determined, again, by measuring changes in storage modulus. Fig. 3a shows the plot of the change in E' over time relative to its value after breakage of the GCs ($\Delta E' = E'_t - E'_{t_0}$). The overall trend is almost identical for the three samples with self-healing agents and shows the rapid effects of the click chemistry polymerization reaction under UV light and its potential to repair damage in the matrix. In the two samples that required reactants to bleed and mix, though, a slightly longer exposure to UV light (15 min instead of 10) was required in order to achieve comparable degrees of reinforcement relative to each system (Fig. S4, ESI†). The self-healing efficiency is highest for the sample with all reactants pre-sorted together, followed by the composite with the monomers mixed together in the tube and the PI dispersed in the matrix, and finally, the sample with monomer reactants

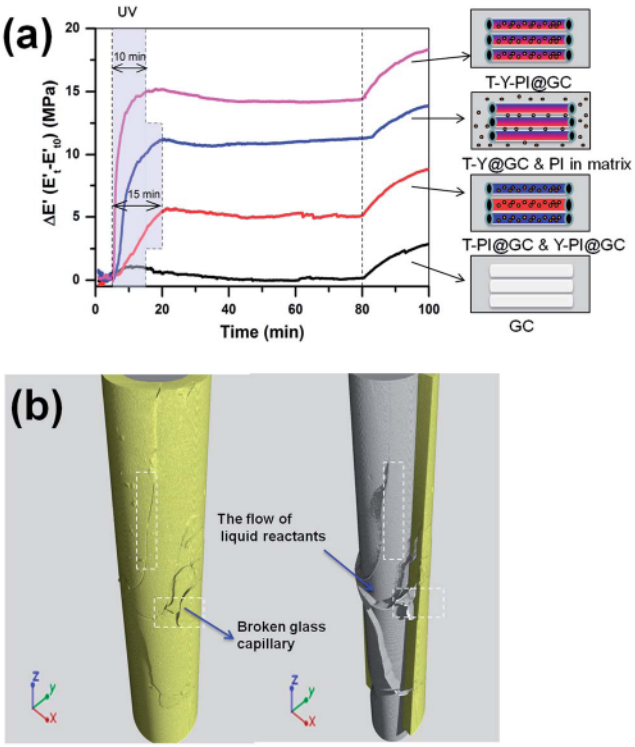

Fig. 3 (a) Comparison of the change in storage modulus ($\Delta E'$) during the self-healing reaction of composites with different configurations. The highest modulus increase is for the composite with three components stored together (T–Y–PI@GC), followed by that in which the PI is dispersed in the matrix and the monomers stored together (T–Y@GC and PI in the matrix) and last the sample with the monomers stored in separate capillaries (T–PI@GC, Y–PI@GC). (b) X-ray tomography of the broken glass capillary (yellow) showing successful capillary-driven bleeding of the self-healing agent (grey) into the crack areas.

(and PI) divided into neighboring GCs. These results highlight the importance of the local concentration T and Y of reactants being close to stoichiometric balance during the reaction, as this represents the balance of the two monomers which ultimately form the cross-linked network. If stored separately, the two monomers are unlikely to flow at the same rate to the damaged area due to viscosity differences, and the reaction itself slows monomer diffusion. Thus, in the latter system, the degree of cross-linking is expected to be lower and consequently to produce a repair with lower modulus ($\Delta E' = 6$ MPa). For comparison, the system containing the two monomers pre-stored together and the PI in the matrix (which might in fact require longer irradiation time to reach completion of the polymerization reaction) results in a higher modulus increase of 12 MPa. It is however a lower value than if all three reactants were stored together. Results so far show that increasing the PI concentration in the matrix leads to higher values of ΔE (Fig. S5, ESI†), presumably as a result of a higher cross-link density due to more availability of the photoinitiator in the crack area.

An implication of the results in Fig. 3a is that the reactants in all the three systems discussed above bleed very effectively to the damaged region of the sample, which is a prerequisite for self-healing.[36,37] We have performed background experiments to detect a possible contribution to bleeding from the cyclic bending deformation induced by the DMA, with the results indicating that mechanical agitation is not required for the reactants to reach and mend cracks in the matrix, thus making the system genuinely self-healing (Fig. S6, ESI†). Instead, bleeding is expected to occur due to the strong capillary action of the microcracks.[9,38,39] This is confirmed by X-ray computed tomography, recently introduced as a powerful technique to characterize self-healing systems.[36,37] 3D reconstructed images of damaged areas in the composites clearly show the filling of cracks at the GC/matrix interface, their small size (<100 μm) providing a strong drive for capillary bleeding (Fig. 3b, S7 and Movie S1†).

In addition to bleeding successfully and reacting rapidly, self-healing materials should be reasonably stable over time. In our system, no reaction would be expected to take place in the absence of UV light even if all three components are stored together. This was confirmed by preparing two identical composite samples with T, Y and PI in the same GCs, testing one immediately after preparation and the other after one-month storage in the absence of UV radiation. The comparison of $\Delta E'$ during the self-healing process, presented in Fig. 4, shows negligible differences in the modulus increase of two materials and indicates that no degradation or premature chemical reaction of the self-healing components occurred. Long term stability and a precise measure of the composites' shelf-life will be the subject of a further study.

The matrix, on the other hand, should have low absorption in the UV range for photoinitiation to occur and the click chemistry reaction to take place through the whole thickness of the sample. Most silicones and polymers without aromatic or unsaturated moieties (*e.g.* polyethylene) fulfill this requirement. This is confirmed for our silicon rubber by UV-Vis spectroscopy and control experiments (Fig. S8 and S9, respectively, ESI†).

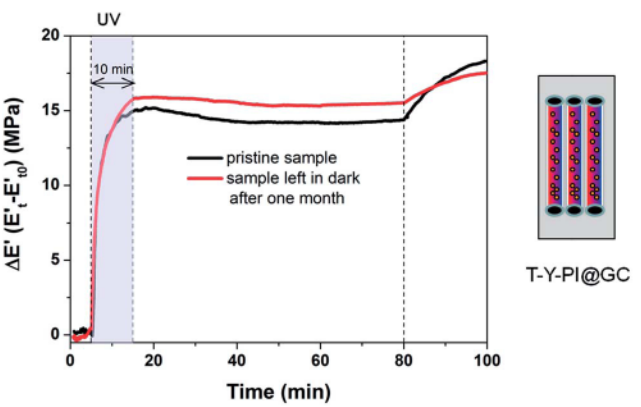

Fig. 4 Plot of change in storage modulus during the self-healing process for a sample tested immediately after preparation and another one tested one month after, showing that no degradation or premature reaction of the click chemistry reactants occurred.

Conclusions

To summarise, in this study a photoinitiated click chemistry reaction was used to repair damage in an elastomer composite. The photoinitiated reaction produces a substantial increase in storage modulus, which is monitored in real time using a DMA. The modulus increase is rapid, up to 30% after exposure for 5 min to the UV source, and reaches completion within only 10 minutes. This improvement is largely due to the successful bleeding of reactants to the crack areas, which is directly confirmed by X-ray tomography. Samples with different storage arrangements were produced and their repair efficiency measured. The results indicate that it is possible to store the reactants in separate GCs and still achieve a significant modulus increase upon exposure to UV light, which implies that multiple self-healing events can take place over time. This photo-initiated reaction might be useful, for example, for remote repairs[13] and in dark environments, but its sensitivity to sunlight limits its spectrum of applications. This limitation is currently being addressed, for example by using UV opaque capillaries to store the reactants. We anticipate that the self-healing approach presented here could be applied to a wide range of polymer composites, but further work is required to reach more significant modulus increases that make the repair of stiffer matrices possible. Additionally, using a different photoinitiator with stronger absorption in the UV-near visible range might increase light penetration into the matrix, making through-thickness curing more efficient and thus improving the self-healing process.

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